Formation of Sultones in Olefin Sulphonation

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Sultones are formed in the sulphonation of unbranched α and internal olefins in the sequence $\beta \rightarrow \gamma \rightarrow \delta$. In the case of α-olefin sulphonation by sulphur trioxide in a short residence time (ca. 60 s) reactor, the $\beta \rightarrow \gamma$ sultone reaction has already gone to completion when the reaction mixture emerges from the reactor. Kinetic data are presented for the $\gamma \rightarrow \delta$ terminal sultone isomerization. In the case of internal olefin sulphonation, formation of γ and δ sultones has not proceeded to a significant extent when the reaction product emerges from the reactor. Kinetic data are presented for the $\beta \rightarrow \gamma$ internal sultone isomerization. Two internal γ-sultones — *cis* and *trans* — are formed, but only one internal δ-sultone, the *trans* isomer. The internal $\gamma \rightarrow$ internal δ sultone isomerizations required forcing conditions (150°C, 3 hr incomplete reactions) or prolonged aging (20–25°C, 21 days; δ sultone still the minor sultone). The *cis* internal γ sultone is more resistant to isomerization than is its *trans* isomer. These reactivity differences are rationalized using arguments developed from that proposed by Bordwell, Osborne and Chapman in 1959 to interpret the effects of methyl substitution on rates of γ-sultone solvolysis.

KEY WORDS: Olefin sulphonation, sultones.

There is now a substantial body of evidence indicating that the initial reaction products from sulphonation of unbranched alkenes are the corresponding β-sultones (1–5), as shown in Scheme 1. In the sulphonation of unbranched alk-1-enes (referred to from here on as α-olefins) the initially formed β-sultone decomposes rapidly to give a product mixture containing the corresponding γ-sultone as a major component, together with the alk-2-ene-1-sulphonic acid (6). With more prolonged aging, the γ-sultone level falls and the corresponding δ-sultone becomes the major component (6).

Less is known concerning the sulphonation of unbranched alkenes with the double bond in non-terminal positions (these alkenes will be referred to from here on as internal olefins). However, the initial formation of β-sultones, with retention of stereochemistry (2), has been established and it is known that stable sultones of the γ and/or δ type are formed subsequently (7).

In this paper we describe an investigation into the nature of the sultones produced by sulphonation of internal olefins, and a study of the changes in sultone composition which occur on aging the sulphonation products of α- and internal olefins.

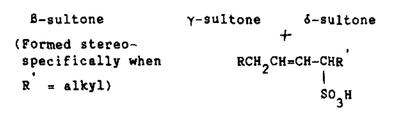
EXPERIMENTAL PROCEDURES

Changes in composition of the olefin sulphonation reaction mixtures were followed by the thin-layer chromatography (TLC) [silica plates, eluted with hexane ether (10:90 v/v), visualization by 50% H_2SO_4 spray and charring at 150°C for 30 min], quantitation being by means of a Zeiss KM3 scanning densitometer. Nuclear magnetic resonance (NMR) spectra were recorded on solutions in deuterochloroform, using a Bruker WM 360 spectrometer.

Sultones from sulphonation of 9-octadecene. The 9-octadecene (78% *cis*, 22% *trans*) was prepared from oleyl alcohol by tosylation followed by reduction with lithium aluminum hydride (8). The sulphonation reactor (FFR) was based on that described by Hulbert, Knott and Cheney (9,10). The sulphonation conditions are shown in Table 1. The sulphonation product (140 g) was left for 21 days at 20–25°C, then neutralized with 5% aqueous sodium hydroxide. The neutralizate was extracted with hexane, and the hexane extract was washed with 50% aqueous ethanol, then eluted through a 2-ft silica column (100–200 mesh) with a hexane/ether (80:20 v/v) mixture.

The eluate (30 g) was separated by preparative high performance liquid chromatography (HPLC) using a Waters Prep 500 instrument (Waters Associates, Milford, MA; stationary phase, silica; liquid phase, hexane/ether 95:5 v/v; elution rate 500 mL/min^{-1}). The sultones isolated in this way (the *trans* 9,12 sultone, 2.5 g; the *trans* 9,11 sultone, 7.5 g; and the *cis* 9,11 sultone, 5.7 g) were recrystallized from methanol. They were characterized spectroscopically as described above and by elemental analyses. *trans*-octadecane-9,12-sultone (mp 52.5°): Found: C, 66.0; H, 10.9%. *trans*-Octadecane-9,11-sultone (mp 32°): Found: C, 64.9; H, 11.0%. *cis*-Octadecane-9,11-sultone (mp 42°): Found: C, 65.2; H, 10.9%. $C_{18}H_{36}SO_3$ requires: C, 65.1; H, 10.9%.

Sulphonation of internal hexadecane. A "localized internal" hexadecene sample (supplied by Gulf Corporation, Houston, TX) was sulphonated continuously using the laboratory scale FFR, under the conditions shown in Table 1. The product emerging from the reactor was collected, over a period of 10 min, into aqueous 10% sodium hydroxide (ca. 100 mL). A sample (21.82 g) of the resulting aqueous neutralizate was added to ethylene glycol (350 mL) and this mixture was heated under reflux, using a modified Dean and Stark apparatus to recover the unreacted olefin by azeotropic distillation. The



Scheme 1. Sulphonation of unbranched olefins.

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TABLE 1

Reaction Conditions for Sulphonation of Olefins Using a Falling Film Reactor (FFR)[a]

	9-octadecene	1-hexadecene	Internal hexadecene
Mole ratio of sulphur trioxide to olefin	1.22:1	1.20:1	1.22:1
Cooling jacket temperature	25°C	45°C	31°C
Concentration of gaseous sulphur trioxide in nitrogen (v/v)	4%	4%	4%
Throughput of olefin	5.8 g.min^{-1}	5.0 g.min^{-1}	7.8 g.min^{-1}
Film residence time	ca. 60 sec[b]	ca. 60 sec[b]	ca. 60 sec[b]

[a] The FFR essentially consists of a vertical glass tube (120 cm long, 7 mm internal diameter) surrounded by a cooling jacket. The material to be sulphonated is supplied to the surface of the top of the tube and is driven downwards by a stream of dry nitrogen, whilst a gaseous sulphur trioxide/dry nitrogen mixture is introduced near the top of the tube.

[b] Measured by a radio tracer method for sulphonation reactions of commercial oleyl alcohol and secondary dodecyl benzene (D.L. Williams, P.S. Jackson and T.C. Pestell, unpublished data) and presumed to have the same value for 9-octadecene sulphonation.

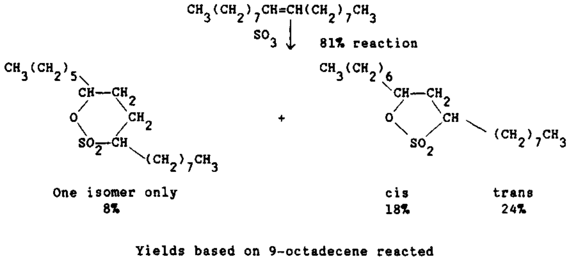
weight of olefin recovered was 1.21 g, corresponding to 5.55% by weight of the aqueous neutralizate. A further sample (50.00 g) of the aqueous neutralizate was mixed with ethanol (100 mL), and the resulting solution was washed with petroleum ether (bp 40–60°C) (3 × 100 mL). The petroleum ether extract was washed with aqueous 50% ethanol (2 × 50 mL) and evaporated down. The weight of petroleum soluble material thereby recovered was 2.28 g, corresponding to 5.56% by weight of the aqueous neutralizate.

RESULTS AND DISCUSSION

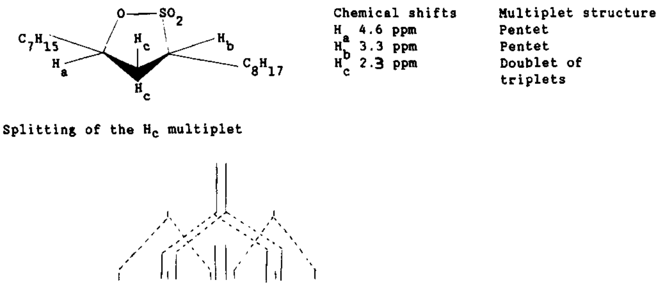
Sultones derived from internal olefins. The symmetrical internal olefin 9-octadecene (78% *cis*, 22% *trans*) prepared from oleyl alcohol by tosylation followed by reduction with lithium aluminum hydride (8), was sulphonated continuously by contacting it with gaseous sulphur trioxide in a laboratory scale falling film reactor (FFR), under the conditions shown in Table 1.

The initial product mixture was allowed to age at 20–25°C for 21 days. Three sultones were detected, and were isolated from the product mixture by a sequence of neutralization, solvent extraction, column chromatography, preparative HPLC and recrystallization. They were identified by their ^{1}H NMR spectra (supported by evidence from mass spectrometry and infrared spectroscopy) as *trans* octadecane 9,12 sultone and *cis* and *trans* octadecane 9,11 sultones. The yields are shown in Scheme 2. All three sultones, when examined by mass spectrometry, showed a molecular ion at m/e 332.

The proton NMR spectrum of the octadecane 9,12 sultone shows two multiplets of equal intensity, at 4.6 ppm and 2.9 ppm. These are assigned to the protons in the 9 and 12 positions, respectively. Our assignment of *trans* stereochemistry to the 9,12 sultone is based on the close similarity between these two multiplets, neither of which shows evidence of equatorial-equatorial splitting. If the sultone had been *cis*, one of these two protons would have been equatorial and the other axial. Other multiplets at 2.2, 1.9 and 1.7 ppm are attributed to the protons in the 10 and 11 positions, but could not be integrated because of their proximity to the large alkyl chain multiplet centered at 1.25 ppm.



Scheme 2. Sulphonation of 9-octadecene.



Chemical shifts	Multiplet structure
H$_a$ 4.6 ppm	Pentet
H$_b$ 3.3 ppm	Pentet
H$_c$ 2.3 ppm	Doublet of triplets

Scheme 3. Proton NMR of *trans* octadecene 9,11 sultone.

The proton NMR spectra of the two octadecane 9,11 sultones are quite different from one another. For the *trans* isomer, the two protons of the ring methylene group are almost chemically equivalent, both being *trans* to one vicinal proton and *cis* to another (Scheme 3). These two methylene protons give rise to a multiplet, centered at 2.3 ppm, which has the appearance of a doublet of triplets. This can be interpreted in terms of an AB pattern further split by two almost equivalent protons, with the outer bands of the AB system being too weak to be detected, as shown in Scheme 3.

In the *cis*-9,11 sultone, the two methylene protons are nonequivalent, one being *trans* and the other being *cis* to two vicinal protons. These methylene protons give rise to two multiplets at 2.9 and 2.3 ppm, each corresponding to one proton. The protons at C9 and C11 have chemical shifts very similar to those of H_b and H_a of the *trans* isomer, but the band structures are more complex, reflecting the greater difference in magnetic environments between the two protons of the C10 methylene group.

The infrared spectrum of the octadecane 9,12 sultone shows an absorption at 915 cm^{-1} typical of δ-sultones. This absorption is absent from the spectra of the octadecane 9,11 sultones, which both show absorptions at 975 and 830 cm^{-1}, typical of γ-sultones. In the *trans* 9,11 sultone spectrum the 830 cm^{-1} absorption is much more intense than the 975 cm^{-1} absorption, whereas for the *cis* isomer, both bands are of similar intensity.

Examination of Dreiding models indicates little difference between the *cis* and *trans* 9,11 sultones in terms of intramolecular steric interactions; in the five-membered ring there is no clear-cut distinction of the axial/equatorial type. In contrast, the 9,12 sultones have cyclohexane-like geometry so that the *trans* isomer (in which both alkyl substituents can occupy equatorial positions) should be thermodynamically favored.

However, under the conditions of our experiment the formation of the 9,12 sultone is kinetically controlled, and the explanation for only one 9,12 isomer being formed must lie in the preferred stereochemistry of the transition state for 9,12 sultone formation. Assuming the final step in formation of a δ-sultone to be the ring closure of a zwitterion, one can readily see from Dreiding molecules that as the carbonium ion center and the -0^- moiety are brought closer together, rotations about the intervening bonds occur, together with rehybridization at the positive carbon center, such that the configurations of the α and δ substituents become increasingly axial-like or equatorial-like. Thus, the argument for the greater thermodynamic stability of the *trans* 9,12 sultone should also apply to the transition states for 9,12 sultone formation, and the *trans* 9,12 sultone should be kinetically favored.

Changes in composition on aging olefin sulphonation products. The α-olefin 1-hexadecene and the internal olefin 9-octadecene were sulphonated continuously by contacting them with sulphur trioxide under the conditions shown in Table 1. Samples of the product mixtures were collected over a period of 5 min (1-hexadecene) or 3 min (9-octadecene) and allowed to age. Changes in composition were followed by thin-layer chromatography, sultone levels being estimated by means of a densitometry technique in which the densitometer response to a spot on the TLC plate is expressed as a peak area. In the case of 1-hexadecene, pure samples of the corresponding γ and δ sultones, hexadecane 1,3 sultone and hexadecane 1,4 sultone, respectively, were available; these standards were applied in known concentrations to the plate at the same time as the sample under investigation, so that by comparison of the densitometer responses the levels of γ and δ sultones in the 1-hexadecane sulphonation products could be estimated. When these experiments were carried out, pure samples of the 9-octadecene-derived sultones were not available. However, since the densitometer response was found to be linear with sultone concentration for the 1-hexadecane-derived sultones, it seemed reasonable to assume that the same would apply for the 9-octadecene-derived product. Thus, the rates of change of sultone levels, although not the absolute levels, could be followed for 9-octadecene sulphonation. The TLC-densitometry method as applied to sultone analysis was originally developed for kinetic studies of hydrolysis of sultones in α olefin sulphonates (A. Lewis, T.D. Finch and D.L. Williams, unpublished data) and was found to be accurate to within 1–2%.

1-Hexadecene sulphonation. In the case of 1-hexadecene sulphonation, the γ-sultone level decreased and the δ-sultone level increased on aging the product mixture at 30°C and at 70°C, as shown in Table 2. From the data, it is clear that the δ-sultone is formed not just from the γ-sultone, but from some other component of the reaction mixture as well, since the difference between initial and final levels for the δ-sultone is almost twice that for the γ-sultone.

It also can be seen from Table 2 that the γ-sultone level had reached its maximum by the time the aging experiments were started, i.e., within 5 min of emergence from the FFR. In a subsequent experiment, 1-hexadecene was sulphonated under similar conditions, and the product emerging from the FFR was collected into aqueous sodium hydroxide. The neutralized product mixture was found to contain ca. 30% of γ-sultone, in good agreement with the $t = 0$ values of Table 2, and indicating that the γ-sultone level had already reached a value close to its maximum before the product mixture emerged from the FFR.

TABLE 2

Changes in Composition of the 1-Hexadecene Sulphonation Product on Aging

Time	Sultone level in sulphonation product (wt%)		Temperature °C
	γ-Sultone	δ-Sultone	
0	No observable change (by visual inspection)	Increasing (by visual inspection)	25
5 min			
15 min			
35 min			
60 min			
0	30.4	10.1	30
1 hr	24.4	16.8	
3 hr	18.1	27.9	
6 hr	15.2	37.2	
72 hr	3.0	60.1	
0	23	17	70^a
15 min	21	26	
30 min	19	32	
1 hr	19	41	
2 hr	12	46	
3 hr	8.5	46	
4 hr	8	47	
4.5 hr	7.5	53	

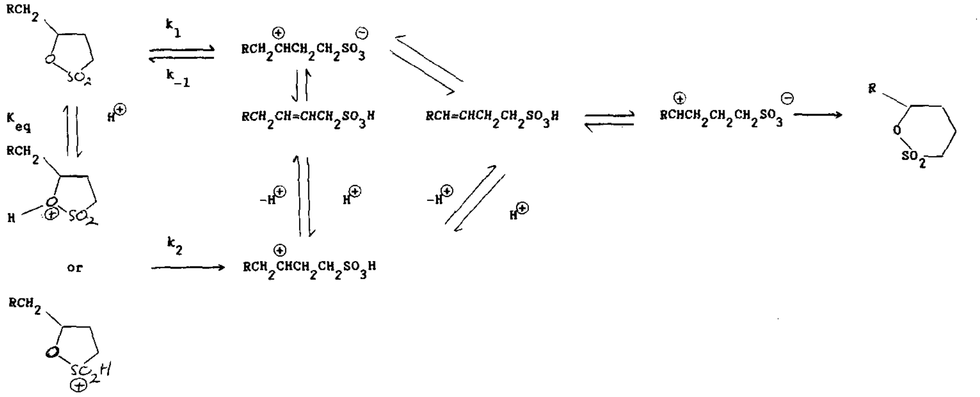
[a] This experiment was carried out on a different sample of 1-hexadecene sulphonation product, which had been stored at ambient temperature for about 30 min after collection from the FFR.

TABLE 3

Attempted First Order Rate Plots for γ-Sultone Decay and δ-Sultone Formations on Aging the 1-Hexadecene Sulphonation Products

Process	Temperature (°C)	Plot	Finding
γ-Sultone decay	30	$\ln(\gamma - 3)^a$ vs t	Smooth curve for $t = 0, 1, 3, 6$ hr
	70	$\ln(\gamma - 6)^b$ vs t	Good straight line $k_{obs} = (1.57 \pm .23) \times 10^{-4}$ sec^{-1} $n = 8^c$, $r = .989^c$
δ-Sultone formation	30	$\ln(60 - \delta)^a$ vs t	Good straight line for $t = 0, 1, 3, 6$ hr $k_{obs} = (3.64 \pm .71) \times 10^{-5}$ sec^{-1} $n = 4$, $r = .998$
	70	$\ln(53.5 - \delta)^b$ vs t	Good straight line for first four points. Large amount of scatter thereafter. $k_{obs} = (2.96 \pm .18) \times 10^{-4}$ sec^{-1} $n = 4$, $r = .9998$

[a] γ_∞ and δ_∞ Values taken as equal to the 72-hr figures.
[b] γ_∞ and δ_∞ Values chosen, by trial and error, to give best linearity.
[c] Two of the data points (at $t = 1$ hr and $t = 3$ hr) are more than three standard deviations from the regression line. Omission of these points lead to: $k_{obs} = (1.50 \pm .03) \times 10^{-4}$ sec^{-1}; $n = 6$; $r = .9999$.



Scheme 4. γ-Sultone decomposition and δ-sultone formation in the α-olefin sulphonation product mixture.

Attempts to obtain first order ratio plots from the data shown in Table 2 revealed an interesting difference between the 30°C and 70°C data. The plots obtained are summarized in Table 3. δ-Sultone formation seems to follow first order kinetics (albeit with much scatter in the latter stages at 70°C) at both temperatures. The rate constants for the two temperatures differ by a factor of 8.1, corresponding to an activation energy of ca. 11 Kcal.mole^{-1}. γ-Sultone decay seems to be less straightforward. It can be seen from Table 3 that γ-sultone decay follows first order kinetics at 70°C, but apparently not at 30°. If a γ_∞ value of 14, very close to the observed $t = 6$ hr value, is taken, then the 30° curve can be made to look more linear to the eye, but the pattern of residuals indicates that the plot is still curved. In any event, in view of a γ value of three being observed at $t = 72$ hr, the use of $\gamma_\infty = 14$ seems totally unjustifiable.

This difference may be rationalized in terms of two pathways for γ-sultone decomposition: an uncatalyzed process and an acid catalyzed process as shown in Scheme 4. Scheme 4 also shows a mechanism for formation of δ-sultone. The rate expression for γ-sultone decomposition, assuming the steps corresponding to k_1 and k_2 to be rated determining and neglecting k_{-1}, is shown in equation [1]:

$$-\frac{d\gamma}{dt} = k_1[\gamma] + k_2K_{eq}[\gamma][H^+] \qquad [1]$$

The source of H^+ is sulphonic acids in the sulphonation reaction mixture, and the level of these will decline as aging proceeds, due to their conversion to δ-sultone. Thus, to the extent that the second term on the right hand side of equation [1] is significant, the reaction rate will decline to a greater extent than predicted for a first order reaction as the reaction proceeds. The catalyzed process will have the lower activation energy and the more negative entropy of activation. Thus, at the higher temperature the $k_1[\gamma]$ term of equation [1] will predominate, leading to a good first order plot, whereas at the lower temperature the $k_2K_{eq}[\gamma][H^+]$ term will

TABLE 4

Changes in Composition of the 9-Octadecene Sulphonation Product on Aging

Time (min)	Sultone level in sulphonation Product (wt%)[a]			Temperature °C
	β-sultone	γ-sultone	δ-sultone	
5	8.00	6.18	< 3%	25
15	7.22	7.14		
30	6.76	8.19		
60	5.33	9.21		
90	4.73	12.25		
2	5.34	9.01		35
5	4.28	9.91		
15	3.58	11.89		
31	2.75	13.59		
45	2.09	15.08		
60	1.83	15.83		

[a] The values given have relative significance only, and can only be compared for the same sultone type, since they are based on the unsubstantiated assumption that the densitometer response factors are the same as for hexadecane-1,3-sultone.

contribute significantly, leading to nonfirst order kinetics, since $[H^+]$ is not constant.

9-Octadecene sulphonation. Aging of the 9-octadecene sulphonation reaction mixture was carried out at 25 and 35°C. In neither case, over a period of 90 or 60 min, respectively, was the δ-sultone formed to a significant extent. The combined γ-sultone level was found to rise, and a component with a TLC R_f value indicating slightly higher polarity than that of the γ-sultones was found to decompose. This component was presumed to be the β-sultone. Internal olefin-derived β-sultones are known to be more stable than their α-olefin-derived counterparts (2,3) and solutions of them, together with other internal-olefin derived sulphonation products, can be stored in inert solvents for several hours at room temperature (3). In further studies currently in progress (which we hope to report more fully at a later date), we have examined reaction products from FFR sulphonation of internal olefins, using NMR to identify β-sultones and to follow their decomposition. The decomposition rates are similar to those reported here based on TLC studies, supporting our assumption that the material whose decomposition is followed is the β-sultone. Table 4 shows the β-sultone and γ-sultone levels measured by TLC. Response factors were assumed, for the purpose of calculation, to be the same as for hexadecane 1,3 sultone; there being no justification for this assumption the figures in Table 4 have no absolute significance, but can be used to analyze the rates of change of β and γ-sultone levels with time.

It is clear from Table 4 that the internal γ-sultones are formed quite slowly and, in contrast to the case with α-olefin sulphonation, their levels continue to increase as the internal olefin sulphonation product is aged following its emergence from the FFR. In a separate experiment a commercial mixture of internal hexadecenes (predominantly with the double bond in the 6, 7 and 8 positions) was sulphonated under similar conditions to those used for 9-octadecene (see Table 1), and the sulphonation product was neutralized immediately by collecting it into aqueous sodium hydroxide as it emerged from the FFR. The aqueous neutralizate was analyzed by azeotropic distillation with ethylene glycol and by extraction with petroleum ether to determine the levels of unsulphonated olefin and total petroleum soluble materials, respectively. The two values were almost identical (olefin 5.55, total petroleum soluble materials 5.56% by weight of the neutralizate), indicating that γ-sultones (which are petroleum soluble) were not present to a significant extent. Thus, in sulphonation of internal olefins under the conditions shown in Table 1, γ-sultone formation does not occur to a significant extent within the residence time of the FFR.

Using the data from Table 4, first order rate plots were obtained for decomposition of 9-octadecene-derived β-sultones and formation of the corresponding γ-sultones, as summarized in Table 5. Evidence that the early stages of the β-sultone decomposition proceed with a rate constant larger than that for the later stages was obtained in the case of the aging experiment at 35°C, as shown in Figure 1. (The 25°C data show a similar,

TABLE 5

First Order Rate Plots for β-Sultone Decay and γ-Sultone Formation on Aging the 9-Octadecene Sulphonation Product

Process	Temperature (°C)	Plot	Finding
β-Sultone decay	25	$\ln\beta$ vs t	$k_{obs} = (1.04 \pm .26) \times 10^{-4}S^{-1}$ $n = 5$, $r = .9913$
	35	$\ln\beta$ vs t	$k_{obs} = (2.65 \pm .55) \times 10^{-4}S^{-1}$ $n = 5$[a], $r = .9939$
γ-Sultone formation, both isomers together	25	$\ln(32 - \gamma)$[b] vs t	$k_{obs} = (5.20 \pm .38) \times 10^{-5}S^{-1}$ $n = 4$[c], $r = .9997$[c]
	35	$\ln(20 - \gamma)$[b] vs t	$k_{obs} = (2.80 \pm .38) \times 10^{-4}S^{-1}$ $n = 6$, $r = .9950$

[a] Data point corresponding to $t = 2$ omitted (see Fig. 1).

[b] γ_∞ Values of 32 and 20 found by trial and error to give best linearity.

[c] Data point corresponding to $t = 60$ omitted, since it deviates from the regression line by more than three standard deviations. Inclusion of this data point leads to: $k_{obs} = (4.87 \pm 1.92) \times 10^{-5}S^{-1}$; $n = 5$, $r = .9789$.

TABLE 6

Effects of Aging on γ and δ Sultone Levels in the 9-Octadecene Sulphonation Product[a]

Aging time (days)	% (Olefin + γ and δ sultones)	% Olefin	% Sultone
0	15.1	10	5.1
1	40.6	8.1	32.5
4	40.5	8.2	32.3
7	38.8	7.0	31.8

[a] Percentages given as weight/weight based on sulphonation product.

but less clear cut, trend.) This is most easily rationalized in terms of one of the β-sultone geometrical isomers being more labile than the other. Consistent with this explanation, it has been reported that *cis*-hexane 3,4 sultone is thermally less stable in solution than is its *trans*-isomer (3).

In order to obtain an assessment of the absolute levels of γ and δ sultones in the 9-octadecene sulphonation product, a further aging experiment was carried out at room temperature. Samples were removed at intervals and neutralized with aqueous sodium hydroxide. The combined (olefin + γ and δ sultone) levels were determined by extraction with petroleum ether and the olefin levels alone were determined by azeotropic distillation with ethylene glycol. Thus the sultone levels could be estimated by difference. The results are shown in Table 6.

After the first day the (γ + δ) sultone level hardly changes. From the rate constant for γ-sultone formation at 25°C (Table 5) it can be calculated that a 24 hr period at 25°C corresponds to 6.5 half-lives, so that after the first day no significant further increase in γ-sultone level would be expected. Formation of δ-sultone is very slow (after 21 days at ambient temperature the 9-octadecene sulphonation product contained only 6% of δ-sultone, *vide infra*), and it therefore follows from the near constancy of the (γ + δ) sultone figures from the first day onwards that the decomposition of internal γ-sultones must also be very slow under the conditions used.

Several qualitative experiments were carried out in order to investigate the effects of aging at higher temperatures. These are summarized in Table 7. From these results we conclude that the decomposition of internal-olefin-derived γ-sultones requires acid catalysis at a temperature around 150°C, and that the *trans*-γ-sultones are considerably more labile than their *cis*-isomers.

The investigation described here reveals several differences between α and internal olefins as regards sulphonation chemistry. These are shown in Table 8. The differences listed can all be ascribed to the effects of an alkyl substituent in the α-position in retarding the rates of ring closure and ring opening. These effects can be rationalized in terms of the principles put forward by Bordwell, Osborne and Chapman (11), to account for the effects of methyl substitution on rates of γ-sultone solvolysis. The basic concept underlying the arguments put forward by these authors is that in ring opening the two atoms between which bond heterolysis occurs cannot separate linearly as in open chain compounds. Instead, separation of these atoms occurs by rotation around the bonds of the ring. Similarly, in ring closure, the two atoms between which bond formation occurs are brought together by rotation, around the preexisting bonds which will form the ring. Steric effects resulting from these rotations bringing substituents on the atoms of the ring, or incipient ring, into greater proximity, lead to significant effects on the reaction rates.

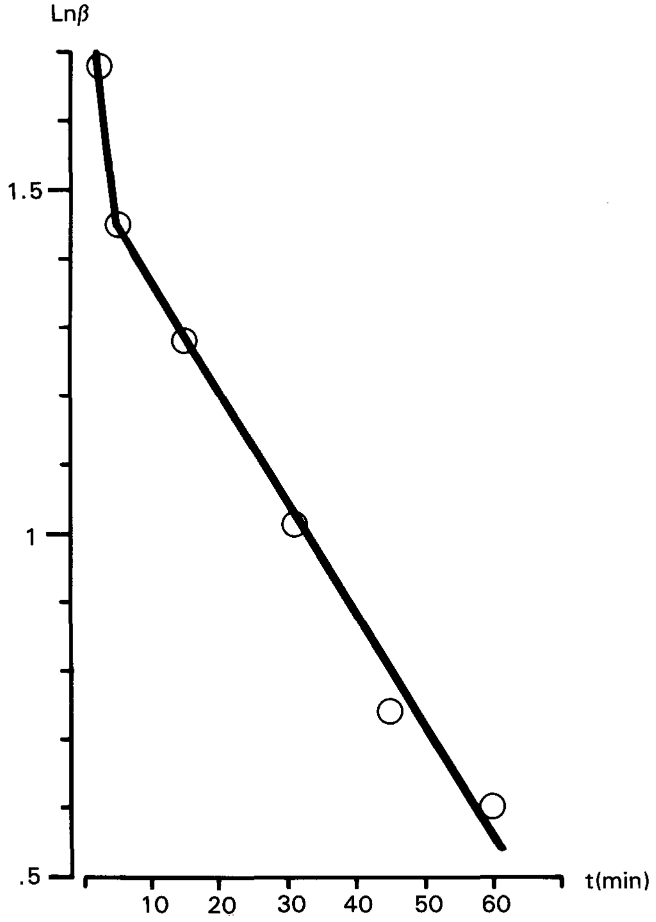


FIG. 1. β-Sultone decay in 9-octadecene sulphonation products at 35°C. Ln (β-sultone) vs *t*.

We defer a discussion of the application of these principles to β-sultone decomposition pending completion of a wider ranging study, currently in progress, of β-sultone decomposition kinetics. The simplest case is that of the δ-sultones. Since these have a staggered conformation, it follows that the ring opening or closing process involves an increase in the degree of eclipsing. This will be greater when there are two alkyl substituents in the ring than when there is only one. Thus, the stability of δ-sultones, and the slower formation of internal olefin derived δ-sultones as compared to α-olefin derived δ-sultones, can be rationalized.

TABLE 7

Effects of High Temperature Aging on Sultone Composition in Products Derived from Internal Olefin Sulphonation

Sample	Aging conditions	Analytical method	Finding
γ-Sultone mixture extracted from hexadecane sulphonation product	Heated alone at 140–150°C for 2 hr.	IR	No detectable change.
	1.8 g heated with 7 drops conc. H_2SO_4 at 170°C for 1 hr.	IR	Major increase in δ-sultone level and decrease in γ-sultone level.
9-Octadecene sulphonation product	Heated at 150°C for 3 hr.	TLC	Major decrease in *trans* γ-sultone spot intensity, but little change in *cis* γ-sultone; major increase in δ-sultone.

TABLE 8

Differences in Sulphonation Characteristics Between α-Olefins and Internal Olefins

	α-Olefins	Internal olefins
β-Sultone stability	Does not survive the residence time in the FFR. $t_{1/2}$ ca. 1 min at 30°C (ref. 2).	Decomposition of one stereoisomer can be followed kinetically over a period of 1–2 hr at 25 and 35°C
γ-Sultone formation	Complete within the residence time of the FFR.	Not formed to a significant extent in the FFR. Formation can be followed kinetically on post-FFR aging.
γ-Sultone decomposition	Can be followed kinetically on post-FFR aging at 30°C and above.	No significant decomposition over several days at ambient temperature.
δ-Sultone formation	Can be followed kinetically on post-FFR aging at 30°C and above. δ-Sultone is the major component of the reaction mixture after 72 hr at 30°C or 4.5 hr at 70°C.	Very slow at ambient temperature. δ-Sultone is still only a minor component of the reaction mixture after 21 days at ambient temperature. Heating for several hours at 150°C is required for δ-sultone to become the major component.

Now consider the γ-sultones. We assume that the bond rotations accompanying the cleavage of the $C(\gamma)-0$ bond will be such that the oxygen atom moves away from, rather than towards, the R group in the γ position so as to minimize non-bonding interactions between that R group and the oxygen atom. It then follows that these bond rotations bring the α-substituent, which is *cis* to the R group in the γ-position, closer to that group. Thus for the *cis* isomer of the internal olefin-derived γ-sultones, ring opening will be less facile than for its *trans* isomer or for the α-olefin derived γ-sultone. As pointed out by Bordwell *et al.* (11), and as can be readily verified with the aid of Dreiding models, rotation about the $\alpha-\beta$ bond causes increased eclipsing between α and β substituents, and this explains why the α-olefin derived γ-sultone is more reactive than either of the internal olefin derived γ-sultones.

The above arguments also apply to ring closure reactions forming the γ-sultones, and can therefore partially rationalize why γ-sultones appear earlier in the case of α-olefin sulphonation than in the case of internal olefin sulphonation. This rationale is adequate, to the extent that the γ-sultones arise from ring closure of γ-zwitterions (or α-sulpho γ-carbonium ions) formed from the breakdown of β-sultones either via rearrangement of β-zwitterions (or α-sulpho-β-carbonium ions) or via (auto)protonation of intermediate β, γ-unsaturated sulphonic acids.

However, there is evidence from solution studies (12) that at least some further reactions of β-sultones may proceed concertedly. In as far as this may apply to the formation of γ-sultones under the conditions used in our study, part of the explanation for the earlier appearance of γ-sultones in α-olefin sulphonation may lie in the relative reactivities of the terminal and internal β-sultones towards rearrangement.

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